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Interactions between Diperoxovanadate and 2-Methyl-imidazole Studied by NMR Spectroscopy

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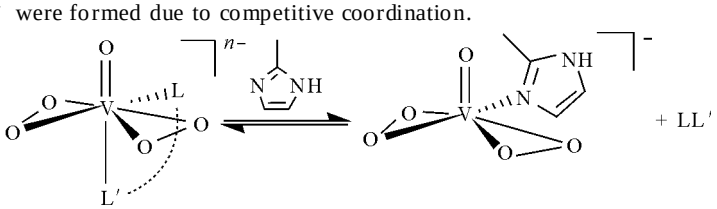
Abstract: To understand the effects of organic ligands on reaction equilibrium, the interactions between diperoxovanadate complexes $[OV(O_2)_2LL']^{n-}$ ($n=1\sim3$; LL′= oxalate, picolinate, 2,2′-bipyridine, and 1,10-phenanthroline) and 2-methyl-imidazole in 0.15 mol/L NaCl ionic medium, which was used to mimick physiological conditions, were explored using multinuclear (^1H, ^{13}C, and ^{51}V) NMR spectroscopy and variable temperature experiments. The experimental results indicated the reactivities of the four diperoxovanadate complexes with 2-methyl-imidazole were as follows: bpV(oxalate) > bpV(picolinate) > bpV(2,2′-bipyridine) > bpV(1,10-phenanthroline). Both the coordination capability and the steric effects of the organic ligands affected reaction equilibrium. New six-coordinated peroxovanadate species $[OV(O_2)_2$(2-methyl-imidazole)$]^-$ were formed due to competitive coordination.



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Introduction

Vanadium compounds play an important role in the biosphere. They were reported to be a new kind of powerful insulin mimic or anticancer agents based on their biological response both *in vitro* and *in vivo* and may be developed into new oral drugs for diabetes or tumor[1-6]. It is therefore not surprising to see that coordination chemistry and biological mechanism of vanadium compounds have recently encouraged great interest. For example, Orvig and co-workers have synthesized and characterized many vanadium(III, IV, V) complexes and studied their insulinomimetic activities[7,8]. Posner and co-workers have synthesized, crystallized, and characterized a series of peroxovanadate complexes and studied their phosphotyrosine phosphatase inhibitory activity[9]. Crans reported that the coordination chemistry of vanadium has great versatility for adjustment of pharmacological characteristics[10]. Pettersson and co-workers used potentiometric and ^{51}V NMR methods to investigate the $H^+ / H_2VO_4^- / H_2O_2/L$ (L = imidazole, L-α-alanyl-L-histidine) systems in detail[11,12]. Conte and co-workers have performed a combined study by using the electrospray ionization-mass spectrometry (ESI-MS), ^{51}V NMR, and density functional calculations to explore the $NH_4VO_3/ H_2O_2/$ histidine-like ligand systems as models to imitate the active sites of haloperoxidases[13,14]. In our previous work[15-23], we have performed experimental and theoretical studies on the interaction between diperoxovanadate and a series of organic ligands in solutions to study their coordinative ways and solution structures. In this work, we used multinuclear (^1H, ^{13}C, and ^{51}V) and variable temperature NMR to study the interaction between a series of diperoxovanadate complexes and 2-methyl-imidazole which contain the imidazole residue of histidine as a start to study the structural characters and reaction properties of diperoxovanadate complexes in 0.15 mol/L NaCl solution as the ionic medium. The reactivity of diperoxovanadate complex is strongly affected by the identity of the ligands; and the results would shed some light on the essence of vanadium-contained enzyme[19].

1 Experimental

1.1 Materials and preparation

The neagents D_2O, H_2O_2 (30 %), NaCl, NaOH, NH_4VO_3, NaC_2O_4, picoline acid (abbr. PA), 2-methyl-imidazole (abbr. 2-Me-Imi), 2,2′-bipyridine (abbr. bipy), and 1,10-phenanthroline (abbr. phen) were analytic grade reagents. The ionic medium 0.15 mol/L NaCl D_2O solution was chosen to represent physiological condition, at 25 ℃ in all NMR experiments.

The four diperoxovanadate complexes are (abbr. bpV) $[OV(O_2)_2LL']^{n-}$ {$n = 1 \sim 3$; LL′ = oxalate (abbr. oxa), picolinate (abbr. pic), bipy, and phen. The corresponding peroxovanadate species are abbreviated as bpV(oxa), bpV(pic), bpV(bipy), and bpV(phen). Their structures are illustrated in Scheme 1. The salutions were prepared on-

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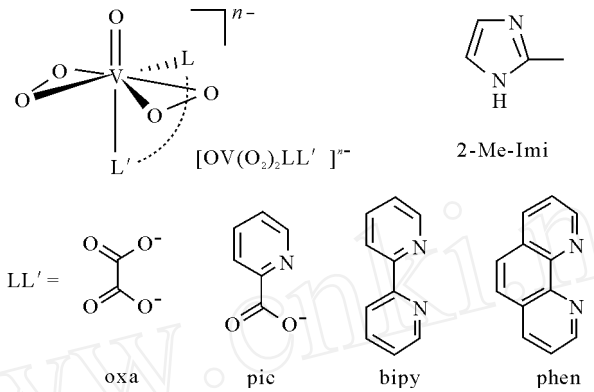
line for the interaction systems NH_4VO_3/ H_2O_2/LL′ (LL′= oxa , bipy , phen , molar ratio 1 ∶5 ∶1) for bpV(oxa) , bpV(bipy) , and bpV(phen) or by NH_4VO_3/ H_2O_2/ PA/ NaOH (molar ratio 1 ∶5 ∶1 ∶1) for bpV(pic) .



Scheme 1 Structures of peroxovanadate species $[OV(O_2)_2LL']^{n-}$ and 2-methyl-imidazole

1.2 Spectroscopies

All spectra were recorded on Varian Unity plus 500 MHz NMR spectrometer , operating at 500.4 MHz for ^1H , 125.7 MHz for ^{13}C and 131.4 MHz for ^{51}V NMR. DSS (3-(trimethylsilyl)-propanesulfonic acid sodium salt) was used as an internal reference for ^1H and ^{13}C chemical shifts. ^{51}V chemical shifts were measured relative to the external standard $VOCl_3$ with upfield shift being considered as negative. Signal-to-noise ratios were improved by a line-broadening factor of 2 or 10 Hz in the Fourier transformation of all ^{13}C or ^{51}V spectra.

2 Results and Discussion

2.1 ^{51}V and ^1H NMR study

There are two peaks in the ^{51}V NMR spectrum of bpV(oxa) in solution locating at δ-692 and -738 , respectively. According to the previous reports , the peak at δ-692 is assigned to $[OV(O_2)_2(L'')]^-$ ($L''= D_2O$ or HOD)[17] , and the peak at δ-738 is assigned to $[OV(O_2)_2(oxa)]^{3-}$ [19]. When 2-Me-Imi was added to bpV(oxa) solution , a new single peak appeared at about δ-746. It was assigned to $[OV(O_2)_2(2\text{-Me-Imi})]^-$. Its intensity increased with the increase in the added quantity of 2-Me-Imi (L″, from 0.5 to 1.0 , 1.5 , and finally 2.0 equivalents) before reaching a maximum , as shown in Fig.1(a) ～(d) and Fig.2(b) . With the crease in addition of 2-Me-Imi , the peak located at δ-692 moved toward high field and disappeared gradually. At the same time , an intermediate peak located at δ-732 was formed , which was assigned to $[V(O_2)_3]^-$. Even if the molar ratio between 2-Me-Imi and vanadate reached 2 ∶1 , the species could not convert to $[OV(O_2)_2(2\text{-Me-Imi})]^-$ completely. There still nemains about 7 % of $[V(O_2)_3]^-$ in the solution. Furthermore , trace $[\{OV(O_2)_2\}_2]^{2-}$ or $[\{OV(O_2)_2\}_2(OD)]^{3-}$ can be ob-

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served in this process, as shown in Fig. 1(b) and (d).

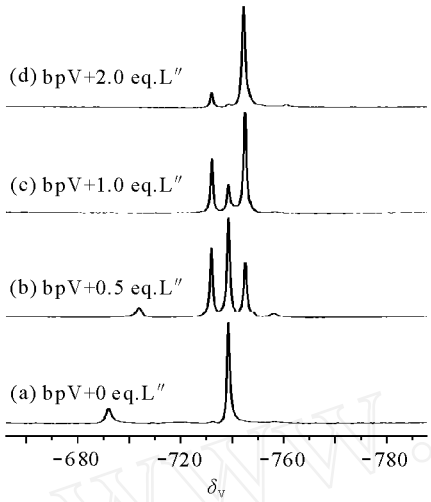

Fig. 1 ^{51}V NMR spectra of the bpV(oxa) and 2-Me-Imi (L″) solutions. The bpV indicates all peroxovanadate species in bpV(oxa) solution with the concentration of 0.20 mol/L.

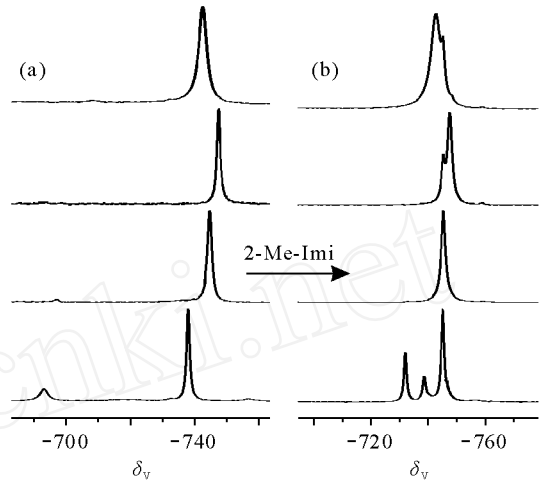

Fig. 2 ^{51}V NMR spectra of the systems of interaction between bpV(oxa), bpV(pic), bpV(bipy) or bpV(phen) and 2-Me-Imi with 1∶1 molar ratio in solution. The total concentration of the vanadate species is 0.20 mol/L in each case.

Analogously, in each ^{51}V NMR spectrum of bpV(pic), bpV(bipy) and bpV(phen) (0.20 mol/L) solution there exists one great peak, located at δ-746, -748, and -742 respectively, as shown in Fig. 2(a). When 2-Me-Imi was added to the bpV(bipy) or bpV(phen) solution, a new single peak appeared at δ-746 which was also assigned to $[OV(O_2)_2(2\text{-Me-Imi})]^-$. Its intensity increases with the increase in the added quantity of 2-Me-Imi. In the system of bpV(pic) and 2-Me-Imi, the peak of $[OV(O_2)_2(2\text{-Me-Imi})]^-$ could not be resolved because it overlaps with the bpV(pic) peak (The formation of new species can be verified by ^{1}H NMR spectrum). Fig. 2 indicates that the reactivities of these complexes with 2-Me-Imi are as follows: bpV(oxa) > bpV(bipy) > bpV(phen).

Since the methyl group in 2-Me-Imi is a single peak in ^{1}H NMR spectrum, it can also be used to measure the reactivities of the four peroxovanadate complexes with 2-Me-Imi. There are two methyl peaks in the ^{1}H NMR spectra of these systems, as shown in Fig. 3. The one located in high field was assigned to the free 2-Me-Imi, and the other located in low field was assigned to the coordinated 2-Me-Imi, i.e. it belongs to the new species formed in the soluiton. Based on the area of methyl peaks, the reactivities of these peroxovanadate complexes are as follows: bpV(oxa) > bpV(pic) > bpV(bipy) > bpV(phen), confirming and supplementing the conclusion from ^{51}V NMR spectra.

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It is worthy to note that the chemical shifts of the free or coordinated 2-Me-Imi are different in different systems. This may be due to their idiographic chemical environment. The variation range of coordinated 2-Me-Imi is smaller to that of free 2-Me-Imi. However, for the 2-Me-Imi and bpV(phen) system, the change of chemical shifts is slight even if their molar ratio varies from 1 ∶1 to 5 ∶1.

Variable temperature ^{51}V NMR was employed to study the influence of temperature on the equilibrium of the reaction between bpV(phen) and 2-Me-imi. The ^{51}V NMR spectra of the mixture of bpV(phen) (0.2 mol/L) and 2-Me-imi with 1 ∶5 molar ratio in the temperature range of 20～65 ℃ are shown in Fig. 4. The following conclusions can be obtained. (1) The quantity of the species $[OV(O_2)_2(2\text{-Me-Imi})]^-$ increases and all of the peaks move towards low field when the temperature increases. The chemical shift of bpV(phen) moves about δ2.6 with the in crease in every 10 ℃, and the chemical shift of $[OV(O_2)_2(2\text{-Me-Imi})]^-$ moves about δ2.4 every 10 ℃. Therefore, their signals can be nesolved better. (2) The trend is reversed when the temperature decreases, as in dieared by the behaviors of the peaks in ^{51}V NMR spectra. The chemical shifts of the peaks are functions of temperature. (3) Both diperoxovanadate species are stable in the temperature range of experiment.

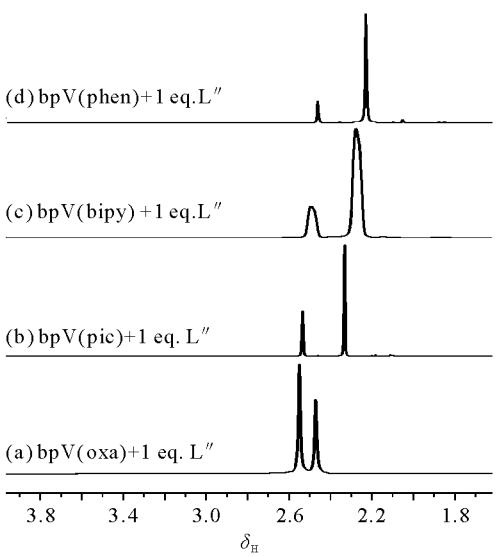

Fig. 3 ^{1}H NMR spectra of the methyl groups of the systems of interaction between bpV(oxa), bpV(pic), bpV(bipy) or bpV(phen) and 2-Me-Imi (L″) with 1 ∶1 molar ratio in solution. The total concentration of the vanadate species is 0.20 mol/L in each case.

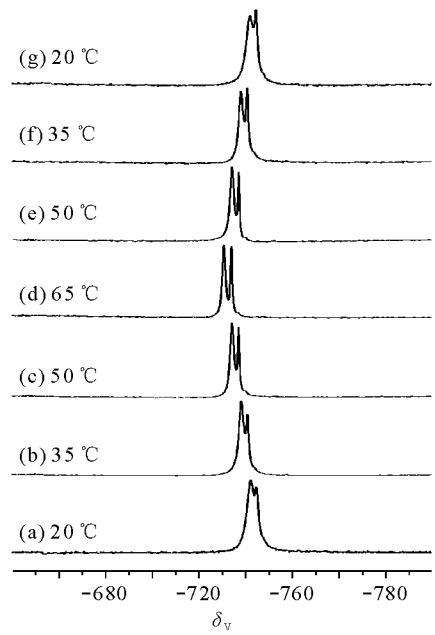

Fig. 4 ^{51}V NMR spectra of the system of interaction between bpV(phen) (0.20 mol/L) and 2-Me-Imi with 1 ∶5 molar ratio at different temperatures. From bottom to top, the temperature increases, and then decreases.

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Table 1 ^{1}H and ^{13}C NMR spectral data of the systems of diperoxovanadate and 2-methyl-imidazole

Systems[a]	Species	Chemical shifts	
		δ_H	δ_C
bpV(oxa) + 2-Me-Imi	$[OV(O_2)_2(oxa)]^-$		175.9, 170.5
	oxa		175.9
	$[OV(O_2)_2(2\text{-Me-Imi})]^-$	2.55(s, 3H, CH_3), 6.98(s, 1H, Imi-H), 7.11(s, 1H, Imi-H)	149.8, 128.9, 119.4, 15.5
	2-Me-Imi	2.47(s, 3H, CH_3), 7.12(s, 2H, Imi-H)	147.2, 121.4, 13.5
bpV(pic) + 2-Me-Imi	$[OV(O_2)_2(pic)]^{2-}$	7.76(s, 1H, Py-H), 8.03(s, 1H, Py-H), 8.18(s, 1H, Py-H), 9.27(s, 1H, Py-H)	171.7, 155.0, 153.5, 144.6, 130.7, 128.1
	pic	7.42(t, J = 5.65 Hz, 1H, Py-H), 7.78～7.86(m, 2H, Py-H), 8.46(s, 1H, Py-H)	175.7, 155.6, 151.0, 140.9, 128.4, 126.3
	$[OV(O_2)_2(Imi)]^-$	2.54(s, 3H, CH_3), 6.98(s, 1H, Imi-H), 7.08(s, 1H, Imi-H)	149.7, 128.9, 119.4, 15.5
	2-Me-Imi	2.30(s, 3H, CH_3), 6.92(s, 2H, Imi-H)	147.9, 123.1, 14.5
bpV(bipy) + 2-Me-Imi	$[OV(O_2)_2(bipy)]^-$	7.24(m, 1H, Py-H), 7.55(t, J = 6.41 Hz, 1H, Py-H), 7.70(m, 1H, Py-H), 7.88(d, J = 7.93 Hz, 1H, Py-H), 8.01(m, 1H, Py-H), 8.10(d, J = 7.93 Hz, 1H, Py-H), 8.34(d, J = 4.88 Hz, 1H, Py-H), 9.37(d, J = 5.19 Hz, 1H, Py-H)	156.9, 156.1, 151.4, 148.6, 144.2, 141.6, 129.0, 128.3, 125.2, 123.5
	bipy	7.19(m, 2H, Py-H), 7.71(m, 4H, Py-H), 7.98(m, 2H, Py-H)	157.2, 151.3, 140.9, 127.0, 124.6
	$[OV(O_2)_2(2\text{-Me-Imi})]^-$	2.49(s, 3H, CH_3), 6.94(s, 1H, Imi-H), 7.02(s, 1H, Imi-H)	149.6, 128.8, 119.2, 15.4
	2-Me-Imi	2.28(s, 3H, CH_3), 6.90(s, 2H, Imi-H)	148.0, 123.3, 14.6
bpV(phen) + 2-Me-Imi	$[OV(O_2)_2(phen)]^-$	7.13(d, J = 8.85 Hz, 1H, Phen-H), 7.22(d, J = 8.85 Hz, 1H, Phen-H), 7.34(m, 1H, Phen-H), 7.48(m, 1H, Phen-H), 7.92(d, J = 8.24 Hz, 1H, Phen-H), 7.97(d, J = 8.24 Hz, 1H, Phen-H), 8.25(d, J = 4.28 Hz, 1H, Phen-H), 9.49(d, J = 4.58, 1H, Phen-H)	156.4, 148.6, 146.1, 143.0, 142.5, 139.6, 131.6, 130.7, 129.2, 128.1, 127.1, 127.2
	phen	6.91(s, 2H, Phen-H), 7.16(dd, J = 7.93, 3.97 Hz, 2H, Phen-H), 7.60(d, J = 7.93 Hz, 2H, Phen-H), 8.56(m, 2H, Phen-H)	151.8, 146.2, 139.2, 130.6, 128.5, 125.8
	$[OV(O_2)_2(2\text{-Me-Imi})]^-$	2.30(s, 3H, CH_3), 6.75(s, 1H, Imi-H), 6.76(s, 1H, Imi-H)	149.0, 128.7, 119.0, 15.3
	2-Me-Imi	2.00(s, 3H, CH_3), 6.60(s, 2H, Imi-H)	147.9, 123.4, 14.7

a. The molar ratio of bpV(oxa) or bpV(pic) and 2-Me-Im is 1∶1, and 1∶2 for bpV(bipy) and 2-Me-Imi, 1∶3 for bpV(phen) and 2-Me-Imi.

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2.2 ^{1}H and ^{13}C NMR data of the systems

The ^{1}H and ^{13}C NMR spectra of the systems of bpV and 2-Me-Imi are listed in Table 1. It shows that the chemical shifts of the coordinated 2-Me-Imi are almost the same in different systems, while those of free 2-Me-Imi are slightly different. In these systems, there are four groups of peaks related to the ligands in both ^{1}H and ^{13}C NMR spectra except for the system between bpV(oxa) and 2-Me-Imi since oxa does not have ^{1}H NMR signals. The four groups of peaks come from the free and coordinated 2-Me-Imi as well as free and coordinated ligands from bpV reactants. In the system of bpV(bipy) or bpV(phen) and 2-Me-Imi, the interaction between them is so weak that much more 2-Me-Imi are needed to achieve enough signal-to-noise ratio for ^{13}C NMR spectra. For simplification, only the ^{13}C NMR spectrum of the system of interaction between bpV(phen) and 2-Me-Imi with 1∶5 molar ratio is given in Fig. 5 as an example.

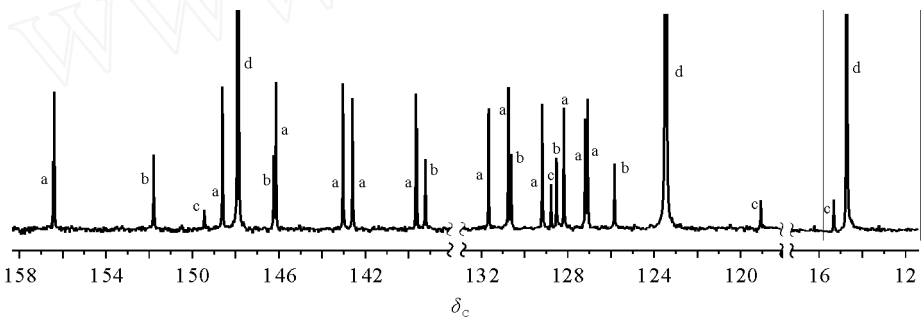

Fig. 5 ^{13}C NMR spectrum of the system of bpV(phen) (0.20 mol/L) and 2-Me-Imi with 1∶5 molar ratio in solution. (a) Coordinated phen; (b) free phen; (c) coordinated 2-Me-Imi; (d) free 2-Me-Imi.

2.3 Reaction modes of the interaction

After analyzing and comparing the ^{1}H, ^{13}C and ^{51}V NMR spectra of the systems of interaction between diperoxovanadate complexes and 2-Me-Imi with different molar ratios, we suggest the possible reaction modes of the systems for bpV(oxa), bpV(pic), and bpV(bipy) as follows (see Scheme 2). (1) The 2-Me-Imi attacks the vanadium of bpV from the opposite site of the terminal oxygen and forms a transition state TS1 (route a). Accompanied by the leaving of water molecule, TS1 turns into the six-coordinated species $[OV(O_2)_2(2\text{-Me-Imi})]^-$ (route b). (2) Similar process can occur between $[OV(O_2)_2(2\text{-Me-Imi})]^-$ and the organic ligands LL′ and forms TS2 (route c) and finally bpV (route d). However, for bpV(phen), the formation of a transition state like TS1 is impossible because of the rigid structure of phen. Therefore, the only way by which 2-Me-Imi replaces phen is the intense collision (route e). Only few 2-Me-Im molecules with high energy can make the reaction happened.

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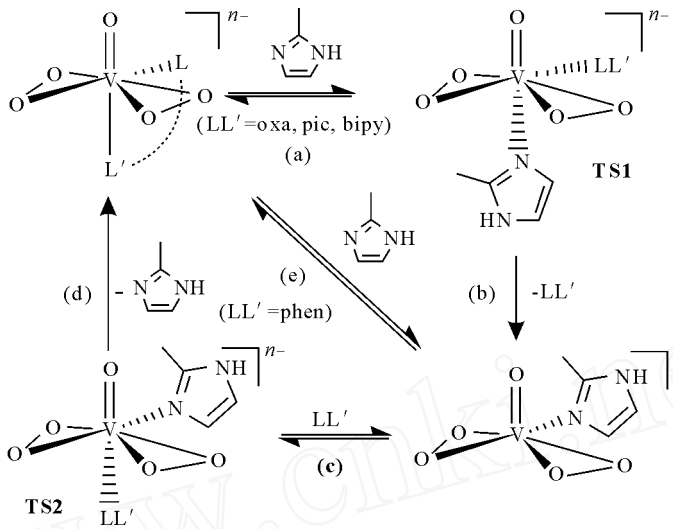

Scheme 2 Possible interaction modes between bpV(oxa), bpV(pic), bpV(bipy) or bpV(phen) and 2-Me-Imi.

Pettersson and co-workers suggested that the reaction ability of organic ligands to diperoxovanadate is: aromatic nitrogen > oxygen[12]. Therefore the order of the reactivities for the four diperoxovanadate complexes with 2-Me-Imi can be deduced to be: oxa (oxygen) > pic (nitrogen + oxygen) > bipy (nitrogen + nitrogen) ≈ phen (nitrogen + nitrogen). With the consideration of the steric effect of phen, the order should be as follows: bpV(oxa) > bpV(pic) > bpV(bipy) > bpV(phen), which is in agreement with our experimental results.

3 Conclusions

Several NMR experimental techniques were employed to study the interactions between diperoxovanadate complexes and the 2-methyl-imidazole in the 0.15 mol/L NaCl D_2O solution. The experimental results indicate that the reactivities of these four complexes with 2-methyl-imidazole are as follows: bpV(oxa) > bpV(pic) > bpV(bipy) > bpV(phen). It is worth noting that the order is the same as their inhibition effect on tyrosine phosphates[24], which means that the histidine**72** near the active center may play an important role in inhibition effect by the coordination of its residue to bpV. Both the coordination capability and the steric effect of the organic ligands affect the reaction equilibrium. The competitive coordination results in the formation of a new six-coordinated peroxovanadate species $[OV(O_2)_2(2\text{-Me-Imi})]^-$.

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双过氧钒配合物与 2-甲基咪唑相互作用的 NMR 研究

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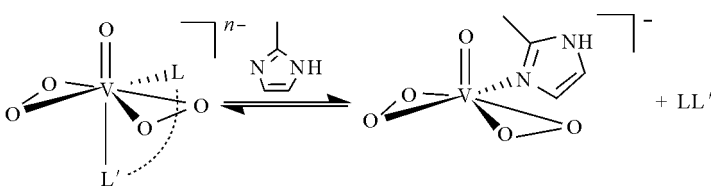
摘　要: 为探讨过氧钒配合物上有机配体对反应平衡的影响, 在模拟生理条件下(0.15 mol/L NaCl 溶液)应用多核(^{1}H, ^{13}C, 和^{51}V)多维(COSY 和 DOSY)NMR 以及变温技术等谱学方法研究双过氧钒配合物$[OV(O_2)_2L]^{n-}$ {n = 1～3, L = oxalate (缩写为 oxa), picolinate(缩写为 pic), bipyridine (缩写为 bipy), 和 1,10-phenanthroline (缩写为 phen), 与它们配位的含钒物种分别缩写为 bpV(oxa), bpV(pic), bpV(bipy)和 bpV(phen)}与 2-甲基咪唑(缩写为 2-Me-Imi)的相互作用, 实验结果表明 2-Me-Imi 与 4 种双过氧钒配合物的反应性从强到弱的顺序为: bpV(oxa) > bpV(pic) > bpV(bipy) > bpV(phen). 研究表明金属中心上配体的配位能力和空间位阻都对反应平衡产生较大的影响, 同时竞争配位的结果导致新的六配位的过氧物种$[OV(O_2)_2(2\text{-Me-Imi})]^{-}$的生成.



关键词: 核磁共振(NMR); 双过氧钒配合物; 2-甲基咪唑; 相互作用

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